Fourth Annual Conference on Carbon Capture & Sequestration

Developing Potential Paths Forward Based on the Knowledge, Science and Experience to Date

Geologic Sequestration (2)

Tests of In-Situ CO_2-Water-Rock Reactions During Carbon Dioxide Injections in Basaltic Rocks: Toward Permanent Sequestration of CO_2

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Outline

1. **Basalts as Potential Host Formations - Overview**

   Permanent Sequestration in Basalt Formations

2. **Experimental Field Tests – Techniques – Results**

   Reservoir Characterization

   Injection Experiments – Single Well Push-Pull Tests

   Geochemical Monitoring
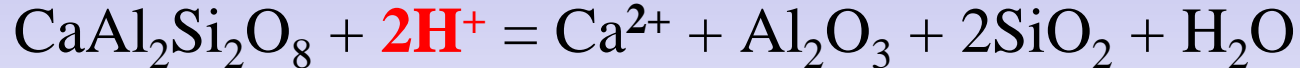
3. **Conclusions**

Acknowlegdments

Objectives

▪ **In-Situ Mineral Carbonation in Suitable Geologic Formations (e.g. Guthrie et al. 2001)**

➤ **Permanence of geologic sequestration over geologic time**

➤ **Effectiveness of CO_2 storage**

➤ **Storage Safety**

➤ **Public Acceptance**

Sequestration Model

1. Dissolution of CO_2 and Dissociation

$$CO_2 + H_2O = H_2CO_3 = \mathbf{H^+} + HCO_3^- = \mathbf{2H^+} + CO_3^{2-}$$

2. Mineral Dissolution

$$Mg_2SiO_4 + \mathbf{4H^+} = 2Mg^{2+} + SiO_2 + 2H_2O$$

$$CaAl_2Si_2O_8 + \mathbf{2H^+} = Ca^{2+} + Al_2O_3 + 2SiO_2 + H_2O$$

3. Mineral Precipitation

$$(Ca^{2+}, Mg^{2+}, Fe^{2+}) + CO_3^{2-} = (Ca, Mg, Fe)CO_3(s)$$

→ Needs source of Base Cations

The release rate of base cations is one of the main rate controlling factors for permanent geologic CO_2 sequestration

Why Basalt Rocks?

Mineral Name	Mineral Formula	Potential CO_2 fixed, kg/m^3 mineral
Plagioclase (anorthite)	$Ca[Al_2Si_2O_8]$	436
Olivine	$Mg_2SiO_4 - Fe_2SiO_4$	2015-1896
Pyroxene (enstatite)	$(Mg,Fe)_2Si_2O_6$	1404
Serpentine	$Mg_6Si_4O_{10}(OH)_8$	1233
Chlorite Group	$(Mg,Al,Fe(II))_{12}[(Si,Al)_8O_{20}](OH)_{16}$	923
Mica group (glauconite)	$(K,Na,Ca)_{1.2-2.0}(Fe(III),Al,Fe(II),Mg)_{4.0}[Si_{7-7.6}Al_{1-0.4}O_{20}](OH)_4.nH_2O$	62
Clay Minerals (Smectite)	$(1/2Ca,Na)_{0.7}(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4.nH_2O$	161

"Natural Analog"

1. Serpentinisation

$$2Mg_2SiO_4 + 3H_2O => Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$$

2. Brucite Dissolution / Magnesite Precipitation

$$Mg(OH)_2 + Mg^{++} + 2HCO_3^- => 2MgCO_3 + 2H_2O$$

Basalt Formation within the U.S.

Columbia River Basalt

164,000 km^2, 174, 000 km^3

K_{mean} Interflow: 10^{-7} m/s / K Interior: 10^{-12} – 10^{-13} m/s

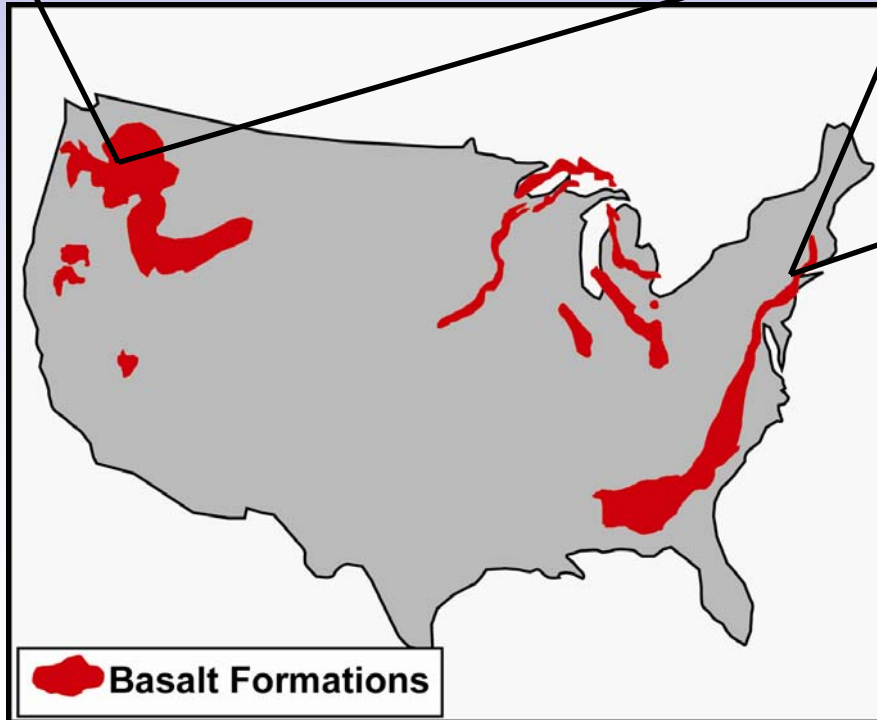Storage Capacity: >100 GtCO$_2$

McGrail et al. 2003; Reidel et al. 2003

Newark Rift Basin (e.g. Palisades Sill)

>100,000 km^2

$K = 10^{-7}$ – 10^{-8} m/s

Effective Porosity: 5 – 8%

Burgdorff & Goldberg 2001; Matter et al. 2005

Ocean Basalt crust (sealed aquifers in upper crust)

Permeability (packer tests): 10^{-10} to 10^{-17} m^2

Porosity: 3 to 15%

Caprock: low-permeability sediments

Fischer 1998; Goldberg 1999

Basalt Formations

Typical Texture of a Flood Basalt
(Reidel et al. 2003; PNNL-14298)
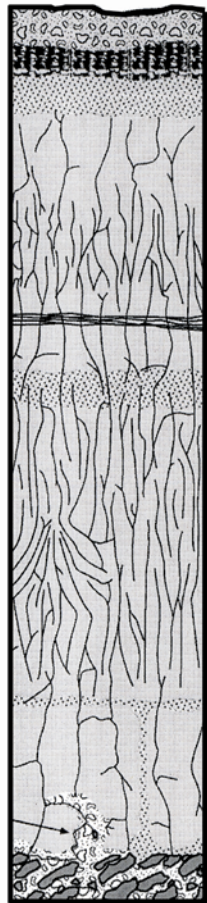
Flow Top Zone
- vesicular to rubbly and/or brecciated basalt
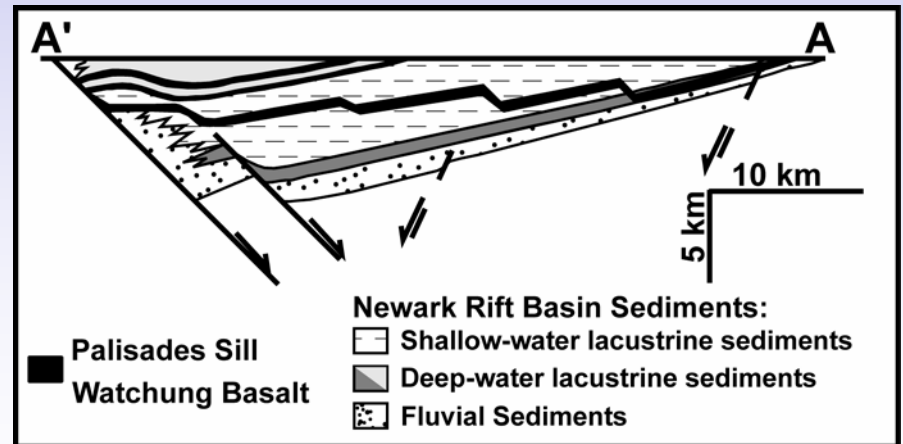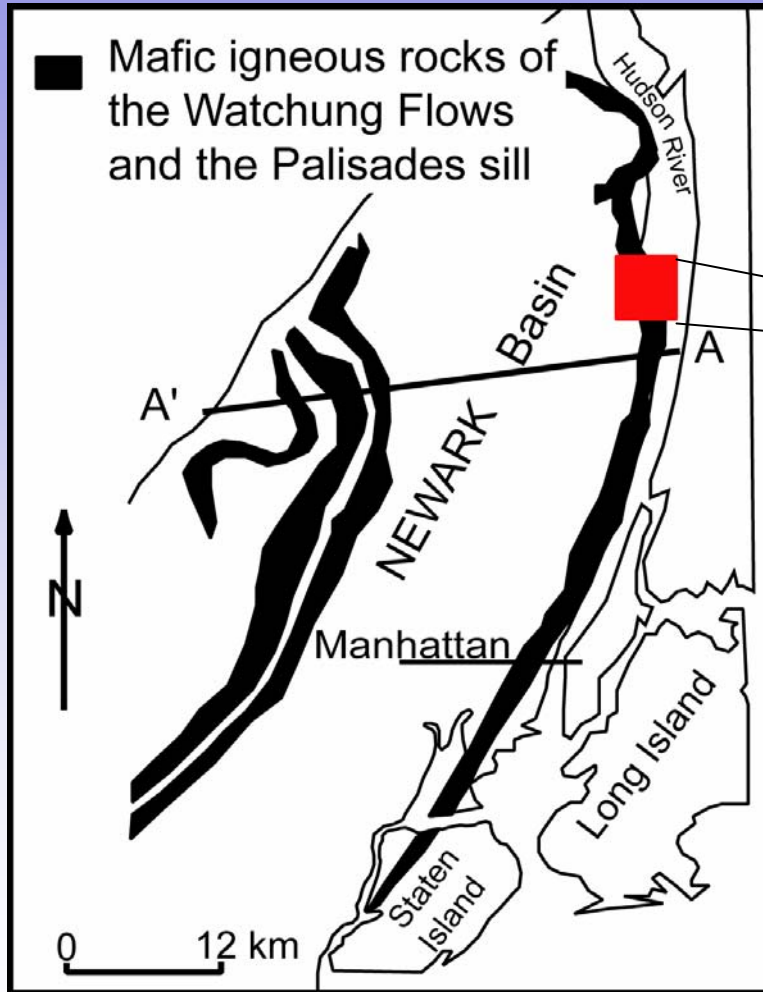
Flow Interior
- entablature and colonnade

Flow Bottom Zone
- can be pillow palagonite complex, hyaloclastite or vesicular to rubbly to brecciated

Aquifer: Flow Top and Bottom Zone (= Interflow Zone); $K_{mean} = 10^{-7}$ m/s

Aquitard: Flow Interior;

**$K = 10^{-12} – 10^{-13}$ m/s**

Test Site – Palisades Sill

CO$_2$ Injection Experiments

Objective

Study the CO$_2$-water-rock reactions, i.e. define the bulk rock dissolution rate or the release rate of base cations, such as Ca^{++}, Mg^{++}

Test Facts

• Single well push-pull test using double packer system

• Injection fluid is a CO$_2$-saturated water (P$_{CO2}$ = 20 atm,

pH 3.5 - 4)

• Chloride and bromide added as conservative tracers

• Injection volume: 2 m^3

• Resting Phase: 7 days

Injection Zone Chacterization
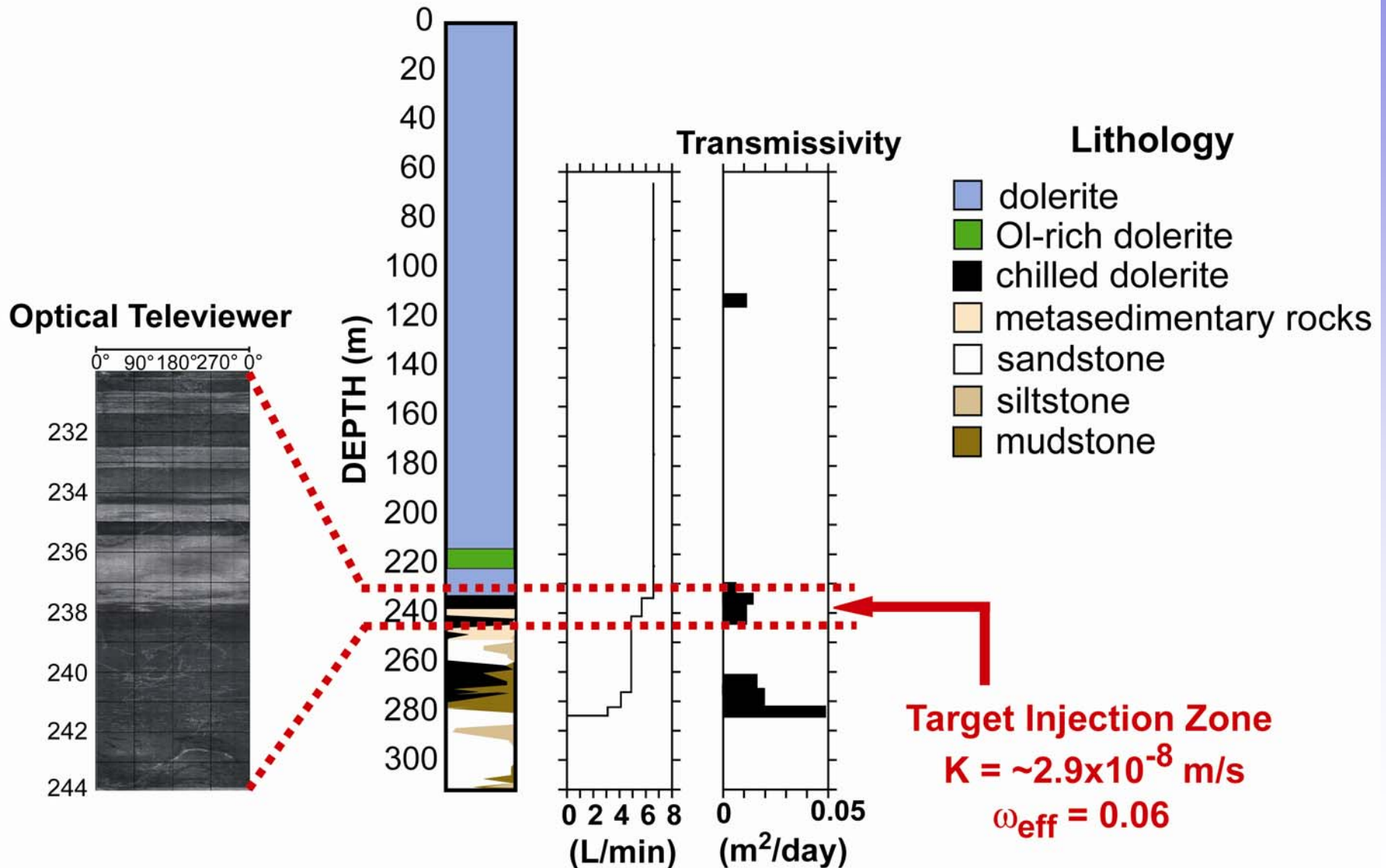
Rock Chemistry - Mineralogy

Chilled Dolerite		Mineralogy (Walker, 1969)
	wt%	
SiO_2	52.13	**Microphenocrysts:**
Al_2O_3	14.70	Olivine $(Mg_{0.8}Fe_{0.2})_2[SiO_4]$
CaO	10.42	Augite $(Ca_{0.4}Mg_{0.46}Fe_{0.14})[Si_2O_6]$
Fe_2O_3	10.12	Bronzite $(Mg_{0.83}Fe_{0.17})_2[Si_2O_6]$
MgO	7.94	Labradorite $(Ca_{0.65}Na_{0.35})[Al_2Si_2O_8]$
Na_2O	2.14	
K_2O	0.69	**Groundmass:**
MnO	0.15	Labradorite $(Ca_{0.65}Na_{0.35})[Al_2Si_2O_8]$
TiO_2	1.28	Augite $(Ca_{0.4}Mg_{0.46}Fe_{0.14})[Si_2O_6]$
P_2O_5	0.17	Magnetite Fe_3O_4
Cr_2O_3	0.07	Ilmenite $FeTiO_3$

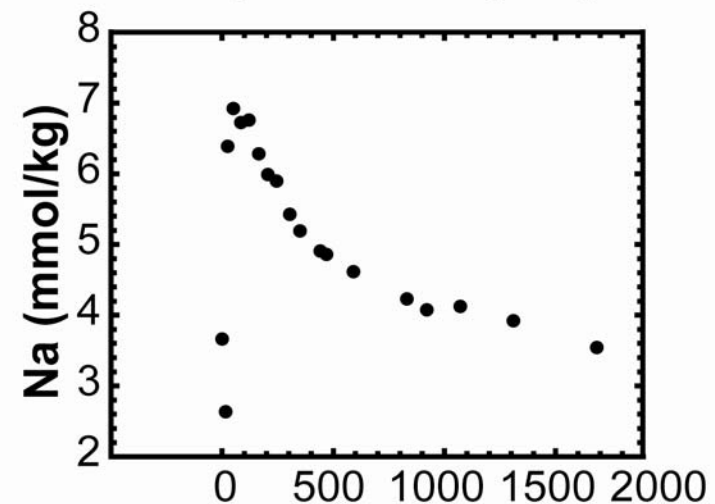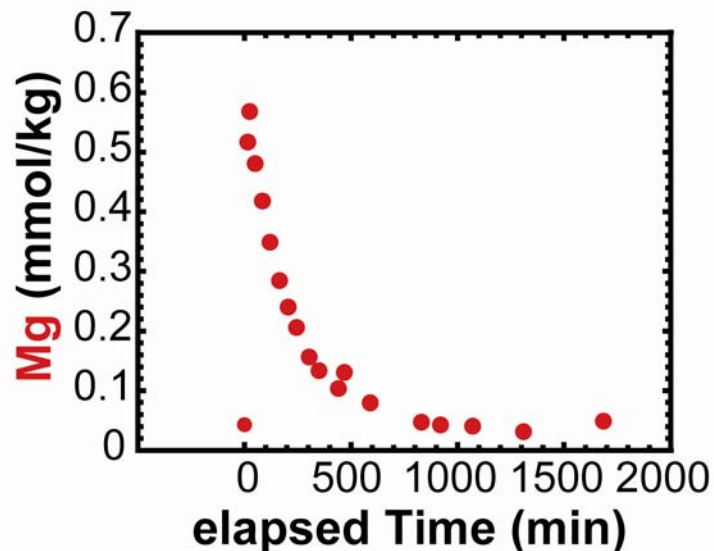# Single Well Push-Pull Tests

Formation Water
+
Tracer + CO$_2$(equil)
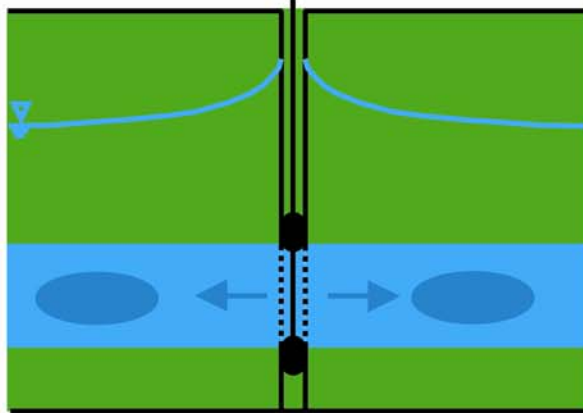
Reaction Test Pumping
+
Final Sampling

Injection Phase

Resting Phase

Pumping Phase

1 to 2 days
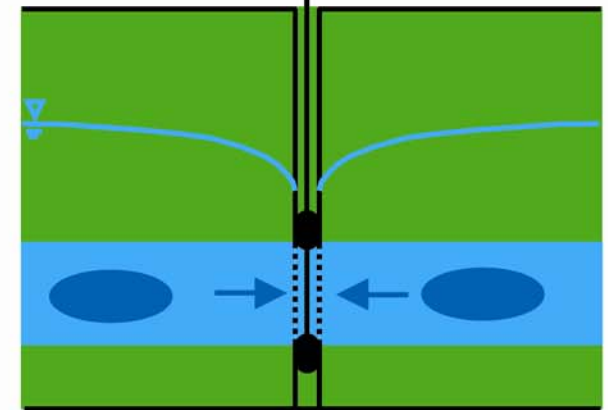
7 days
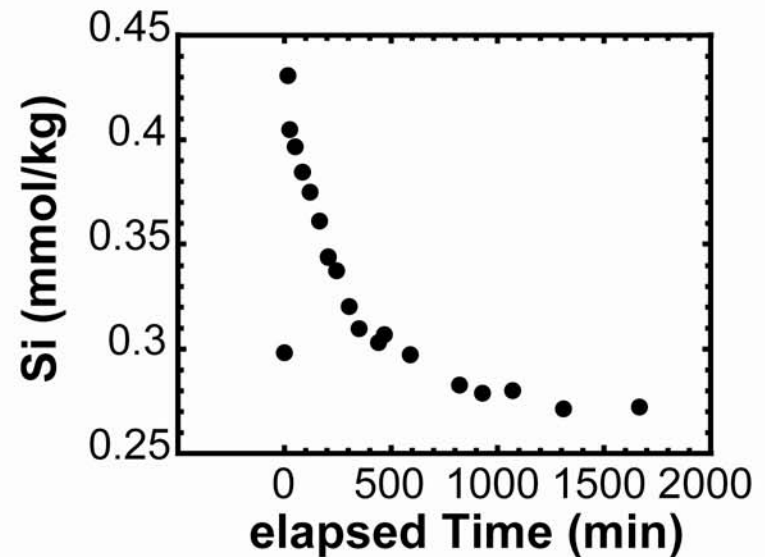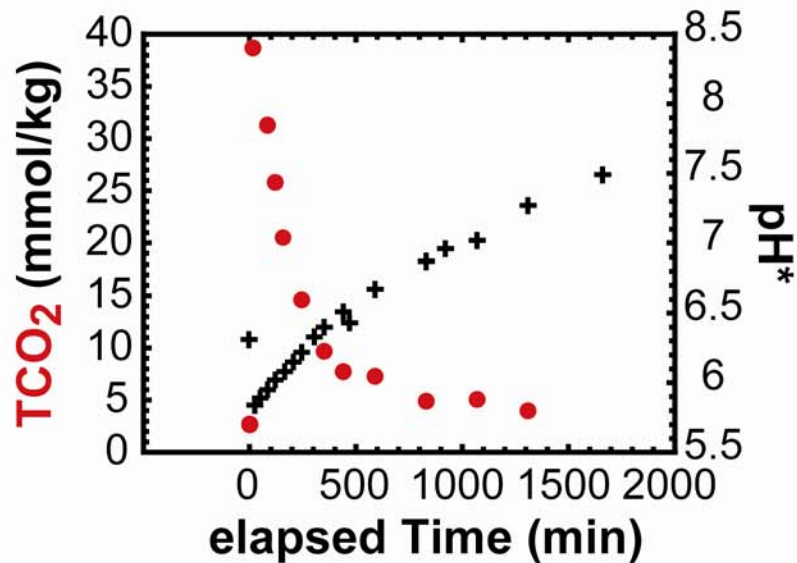
5 to 7 days
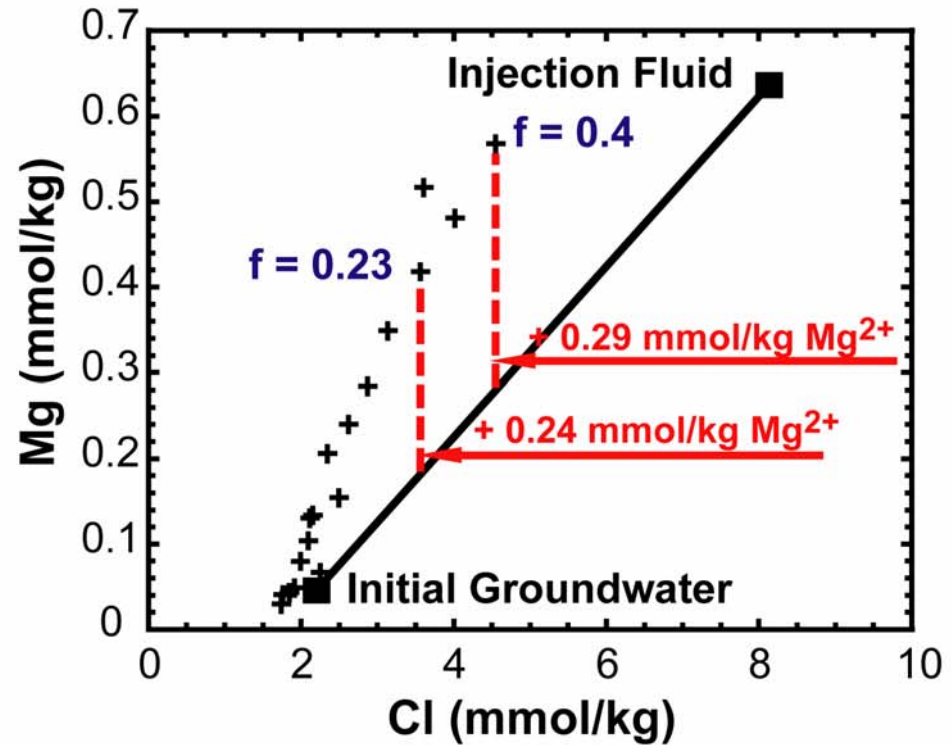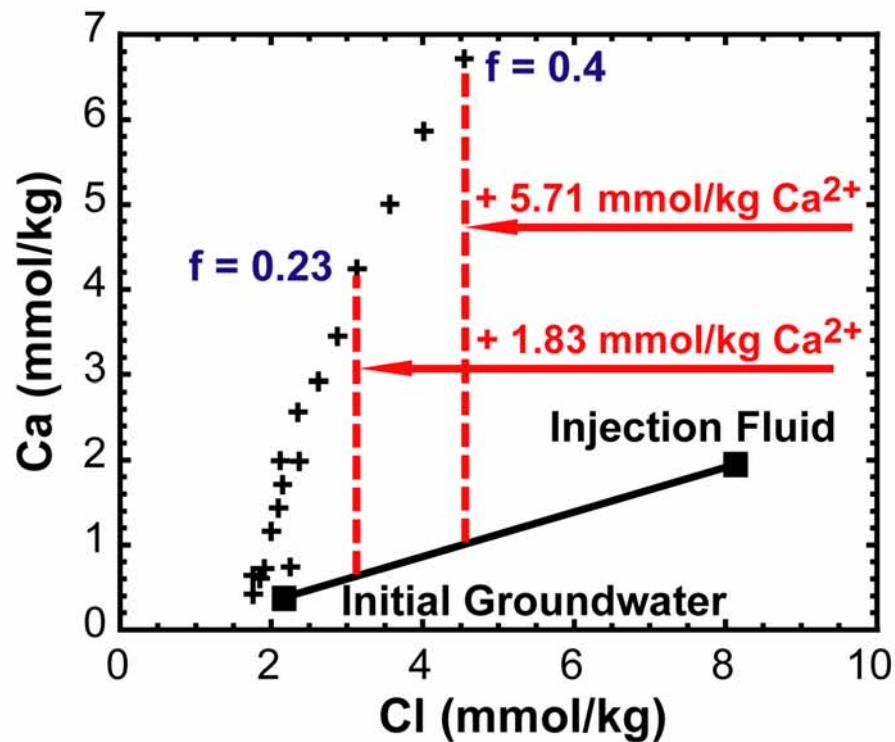
Chemical Monitoring – Breakthrough Curves
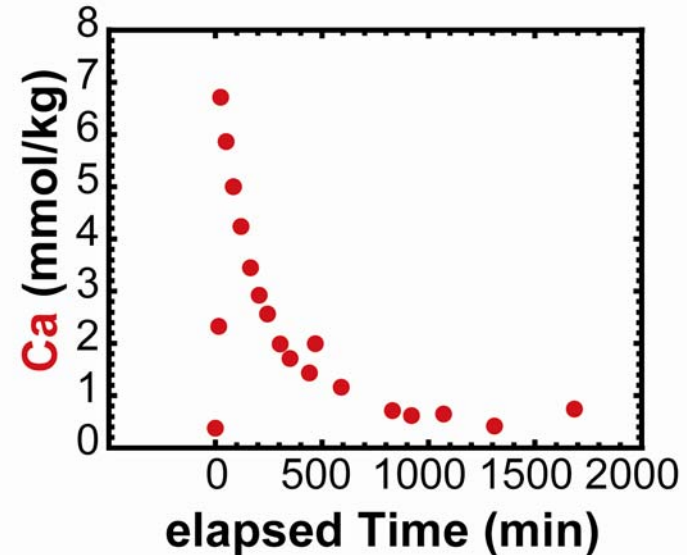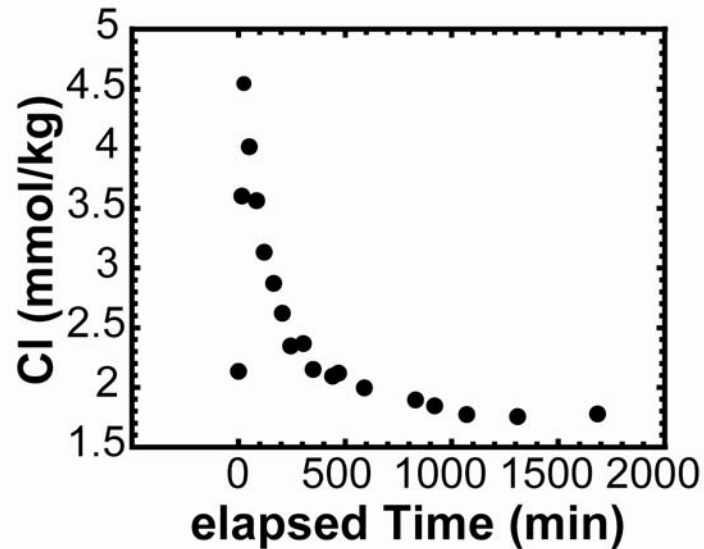
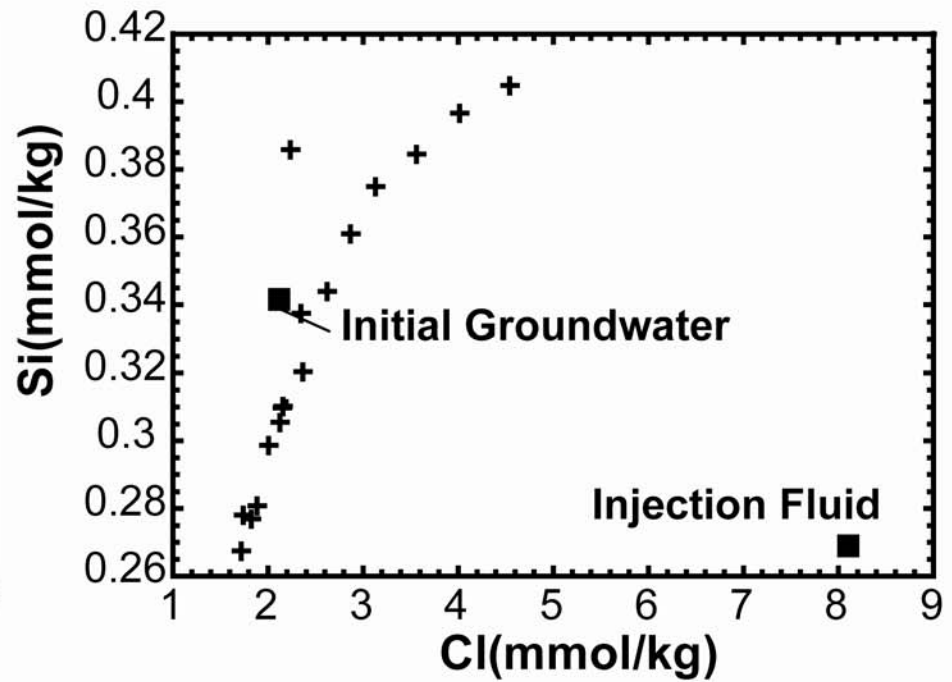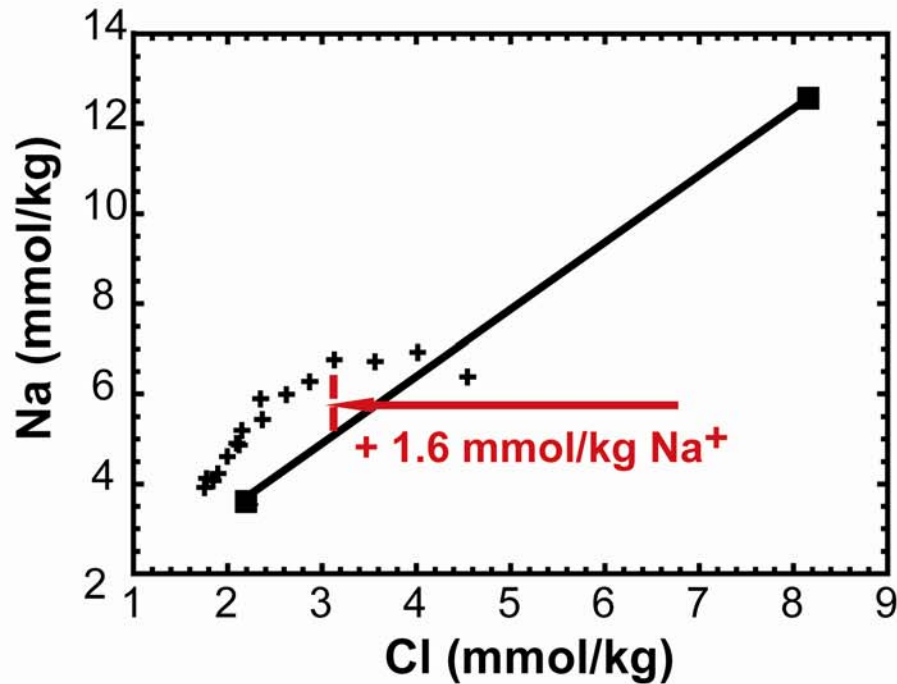# Chemical Monitoring – Breakthrough Curves

Rock – Water Reactions (Acid Neutralization)

Rock – Water Reactions (Acid Neutralization)

Conclusions

- Ca, Mg silicate rocks, such as the Palisades dolerite are highly reactive under acidic (pH 3 to 4) conditions.

- Field-based estimates of the in-situ bulk rock dissolution or release rates (based on the Ca^{++} release) range from 9.8×10^{-3} mol/m^2/day to 6.2×10^{-4} mol/m^2/day.

- Fracture spacing, fracture aperture and fracture porosity were estimated based on borehole geophysical measurements and used to calculate rock surface area, which was then included in the dissolution rate calculations (see Steefel and Lasaga, 1994).

- Since parameters measured at lab scale do not apply at field scale, field experiments on intermediate to large scale are needed to understand CO_2-water-rock reactions.

- Basalt formations can provide the porosity and permeability as well as the geochemical reactivity needed to permanently sequester large amounts of the current CO_2 emission.